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KONINKRIJK DER NEDERLANDEN

Bureau voor de Industriële Eigendom

This is to declare that in the Netherlands on January 1, 2004 under No. PCT/NL2004/00029,
in the name of:
DSM IP ASSETS B.V.
in Heerlen, the Netherlands and
Joseph Arnold Paul Maria SIMMELINK
in Sittard, the Netherlands and
Jacobus Johannes MENCKE
in Maastricht, the Netherlands and
Roelof MARISSEN
in Born , the Netherlands and
Martinus Johannes Nicolaas JACOBS
in Heerlen, the Netherlands
an international patent application was filed for:
"Process for making high-performance polyethylene multifilament yarn",
and that the documents attached hereto correspond with the originally filed documents.

Rijswijk, February 3, 2005

In the name of the president of the Netherlands Industrial Property Office

Mrs. C.M.A. Streng

PROCESS FOR MAKING HIGH-PERFORMANCE POLYETHYLENE MULTIFILAMENT YARN

The invention relates to a process for making high-performance polyethylene multifilament yarn comprising the steps of

a) making a 3-25 mass% solution of ultra-high molar mass polyethylene having an intrinsic viscosity as measured on solutions in decalin at 135°C of between about 8 and 40 dl/g, in a solvent;

b) spinning of the solution through a spinplate containing at least 5 spinholes into an air-gap to form fluid filaments, while applying a draw ratio DR_{fluid};

c) cooling the fluid filaments to form solvent-containing gel filaments;

d) removing at least partly the solvent from the filaments; and

e) drawing the filaments in at least one step before, during and/or after said solvent removing, while applying a draw ratio DR_{solid} of at least 4.

The invention further relates to a high-performance polyethylene multifilament yarn, and to semi-finished or end-use products containing said yarn, especially to various kinds of ropes and ballistic-resistant composites.

Such a process is known from WO 01/73173 A1. A polyethylene multifilament yarn with a tensile strength of 4.0 GPa for a yarn containing 60 filaments is decribed in this patent publication, which was made by a continuous process comprising the steps of

a) making a solution of 8 mass% of ultra-high molar mass polyethylene homopolymer having an intrinsic viscosity of 27 dl/g in mineral oil;

b) spinning of the solution through a spinplate containing 60 spinholes of about 1 mm diameter and L/D of 40 into an air-gap of about 3.2 mm to form fluid filaments, while applying a draw ratio DR_{fluid} of 15;

c) cooling the fluid filaments in a water quench bath to form solvent-containing gel filaments;

d) removing the solvent from the filaments by extraction with trichlorotrifluoroethane; and

e) drawing the filaments in five steps before, during and after removing the solvent applying a draw ratio DR_{solid} of 36.5.

A high-performance polyethylene multifilament yarn is herein understood to mean a yarn containing at least 5 filaments made from ultra-high molar mass, or ultra-high molecular weight, polyethylene having an intrinsic viscosity (IV, as

measured on solution in decalin at 135°C) of at least about 4 dl/g (UHPE), the yarn having a tensile strength of at least 3.0 GPa and a tensile modulus of at least 100 GPa (hereinafter also simply referred to as strength or modulus). Such HPPE yarns have a properties profile that make them an interesting material for use in various semi-finished and end-use products, like ropes and cords, mooring lines, fishing nets, sports equipment, medical applications, and ballistic-resistant composites.

Within the context of the present invention a yarn is understood to be an elongate body comprising multiple individual filaments having cross-sectional dimensions much smaller than their length. The filaments are understood to be continuous filaments; that is being of virtually indefinite length. The filaments may have cross-sections of various geometrical or irregular shapes. Filaments within a yarn may be parallel or entangled to one another; the yarn may be linear, twisted or otherwise departed from a linear configuration.

It is well known in the field of fibres and yarn technology that a multifilament yarn shows lower tenacity or tensile strength than the strength as measured on its constituent individual filaments. In general, the more filaments a yarn contains, the lower its tensile strength (breaking strength per unit of cross-sectional area, e.g. N/m^2 or Pa).

Figure 1 confirms the said decrease in tensile strength with increasing number of filaments in a yarn for some commercially available HPPE yarns; by showing tensile strength (TS) data for the indicated Spectra® and Dyneema® grades, as collected from brochures and web-sites of the respective producers and plotted versus the logarithm of the number of filaments (n) in the yarn.

It is furthermore well known, that spinning of high-strength multifilament yarn becomes increasingly difficult the higher the number of filaments in the yarn as spun, one of the likely reasons being differences in spinning and drawing conditions and subsequently in tensile properties occurring between filaments. For a polyethylene multifilament yarn spinning process to be commercially viable on industrial scale, it is important that such process can be run continuously without interruptions and with high throughput rate, with a high number of filaments in the as-spun yarn. The skilled person further knows, often from own experience, that a process, which results in a polyethylene monofilament of very high strength on a small scale, like reported in JP 59/216913 A or in EP 0200547 B1, will not simply result in production of multifilament yarn of similar strength if applied as such on an industrial scale. Assembling a multifilament yarn from a plurality of monofilaments or from yarns

containing few filaments may theoretically present an alternative route, but such route appears technically and economically not feasible.

In many of the above-mentioned applications for HPPE yarn, the strength of the yarn applied is a critical property determining performance. There is thus a constant need in industry for HPPE multifilament yarn having improved tensile properties, and for a process that enables production of such high tensile strength yarn on industrial scale.

According to the present invention, this is provided by a process wherein in step b) a fluid draw ratio $DR_{fluid} = DR_{sp} \times DR_{ag}$ of at least 150 is applied, wherein DR_{sp} is the draw ratio in the spinholes and DR_{ag} is the draw ratio in the air-gap, with DR_{sp} being greater than 1 and DR_{ag} at least 1.

With the process according to the invention a HPPE multifilament yarn is obtained that has higher tensile strength than any known HPPE yarn containing at least 5 filaments, especially an as-spun yarn; more specifically a HPPE multifilament yarn containing n filaments is obtained that has a tensile strength of at least $5.8*(n^{-0.065})$ GPa, wherein n is at least 5.

It is surprising that the process according to the invention results in yarn with improved tensile properties, because processes for making HPPE multifilament yarn comprising a step with a certain draw ratio, also referred to as stretch ratio, applied to filaments in the fluid state (DR_{fluid}) are described in numerous publications. For example, in EP 0472114 B1 a process is disclosed, wherein a minimum draw ratio DR_{fluid} of at least 3 is applied in an air-gap of several centimetres. For making 16- or 19-filament yarn from polyethylene of intermediate molar mass (preferably 300-700 kg/mol) a DR_{fluid} of 10-50 is indicated as a preferred range for reaching optimum properties. EP 0200547 B1 suggests that the optimum DR_{fluid} lies in the range from 6 to 200, depending on the concentration of the solution and operation conditions. This publication, however, only discloses spinning of a monofilament in its examples. In WO 01/73173 A1 it is indicated that the draw ratio DR_{fluid} is preferably at least 12; but a 16-filament yarn made with a DR_{fluid} of about 34 had tensile properties lower than a yarn made with a DR_{fluid} of about 23. None of these publications discloses or suggests applying a minimum draw ratio DR_{fluid} of 150, resulting from drawing in both the spinhole and the air-gap to increase multifilament yarn strength.

Another advantage of the process according to the invention is that the draw ratio DR_{sp} can be set by choosing the geometry of the spinholes, which can be much better controlled than drawing in an air-gap. A further advantage is that the

temperature during drawing in the spinholes can be better controlled than in the air-gap, which further reduces differences in processing conditions between filaments. It is known that even small differences in the temperature of a polyethylene solution will strongly affect its rheological properties, and thus drawing behaviour. Still a further advantage is that a larger air-gap can be applied, which is less critical to small fluctuations, for example resulting from movement of the surface of the quench bath. A distinct advantage of the process of the invention is thus an improved processing stability, and more consistency in properties between filaments. These advantages become more apparent with increasing number of filaments that are being spun. Preferably, the number of filaments in the yarn is at least 10, 50, 100, 150, 200 or even at least 300. For practical reasons, handling during spinning and drawing becomes increasingly difficult, the number of filaments is preferably at most about 5000.

A spinplate is also called spinneret in the art, and contains multiple spinholes, also called orifices, dies, apertures, capillaries or channels. The number of spinholes determines the maximum number of filaments in as-spun yarn. The spinhole has certain geometry in length and transverse directions, and is preferably of circular cross-section to result in highest strength, but also other shapes are possible, if other forms of filaments are desired. Within the context of the present invention the diameter is meant to be the effective diameter; that is for non-circular or irregularly shaped spinholes the largest distance between an imaginary line connecting the outer boundaries.

Within the context of the present invention, a draw ratio of greater than 1 in a spinhole is applied, if the polyethylene chains in the solution are oriented as a result of an elongational flow field in the spinhole and the orientation so obtained is not subsequently substantially lost as a result of relaxation processes. Such molecular orientation, and thus a draw ratio greater than 1 results if the solution flows through a spinhole having a geometry comprising a contraction zone, that is a zone with a gradual decrease in diameter from diameter D_0 to D_n with a cone angle in the range 8-75°, and wherein the spinhole comprises a zone of constant diameter with a length/diameter ratio L_n/ D_n of from 0 to at most 25 downstream of a contraction zone. L_n is the length of a zone with constant diameter D_n; which length should not be above $25D_n$ to prevent that the molecular orientation introduced in the contraction zone is substantially lost again.

With cone angle is meant the maximum angle between the tangents of opposite wall surfaces in the contraction zone. For example, for a conical or tapered contraction the angle between the tangents is a constant, i.e. the cone angle; for a so-called trumpet type of contraction zone the angle between the tangents will decrease with decreasing diameter; whereas for a wineglass type of contraction zone the angle between the tangents will pass through a maximum value.

At a cone angle of greater than 75° flow instabilities like turbulence are likely to occur, which would not result in the desired elongational orientation of the molecules. Preferably, the cone angle is at most 60°, at most 50°, more preferably at most 45°. Too small a cone angle is less effective in orienting the polymer molecules, and would result in very long spinholes. Preferably, the cone angle is from at least 10, more preferably at least 12°, or even at least 15°.

The draw ratio in the spinhole is represented by the ratio of the solution flow speeds at the initial diameter or cross-section and the final diameter of the spinhole; which is equivalent to the ratio of the respective cross-sectional areas, or the ratio between the square of the initial and final diameters in case of cylindrical holes, that is $DR_{sp} = (D_0/D_n)^2$.

Preferably, the draw ratio in the spinholes is at least 2, 5, 10, 15, 25, 40 or even at least 50, because extent and conditions of drawing can be well controlled in the spinholes. In addition, a higher draw ratio in the spinhole, with constant draw ratio in the air-gap, has been found to result in higher tensile strength of the yarn obtained. In a special embodiment, the DR_{sp} is larger than DR_{ag} for the same reason.

The spinhole may further comprise a zone of constant diameter D_n downstream of a contraction zone, this zone having a length/diameter ratio L_n / D_n of at most 25, preferably at most 20, at most 15, 10, or even at most 5. The length of this zone can also be 0; such a zone need not be present in the spinhole. The advantage of the presence of this constant diameter zone is a further improved stability of the spinning process, but its length should be limited in order that the molecular orientation introduced in the contraction zone is not substantially lost.

It is noted that in WO 01/73173 A1 a process is disclosed that applies a spinplate with spinholes having a tapered inflow zone with a cone angle of about 90° as deduced from figure 2, and with a downstream zone of constant diameter with a length/diameter ratio L/D greater than10, preferable greater than 25 or 40 (40 and 100 in the examples). In such a spinhole, no effective molecular orientation will occur. According to above definition, the draw ratio in this known spinhole is thus 1.0.

The final diameter of the spinhole may vary, depending on total draw ratio and desired filament thickness. A suitable range is from 0.2 to 5 mm, preferably the final diameter is from 0.3 to 2 mm.

The spinholes may also contain more than one contraction zone, each optionally followed by a zone of constant diameter. In such case similar features relate to each zone as discussed above.

In a special embodiment of the process according to the invention, the spinholes in the spinplate further comprise an inflow zone of constant diameter of at least D_0, and of length L_0 with a ratio L_0 / D_0 of at least 5. The advantage of such zone is that the polymer molecules in the solution can at least partly relax such that pre-orientation originating from upstream flow fields can diminish or disappear. This is especially advantageous in case of a high number of spinholes, requiring complex feed channels that may result in quite different flow histories and degrees of pre-orientation per spinhole. The longer this inflow zone, the more relaxation can occur, therefore, the inflow zone preferably has a L_0 / D_0 of at least 10, 15, 20, or even 25. It should be noted that the flow speed in this zone is significantly lower than after passing the contraction zone, and for relaxation to occur a relatively small L_0 /D_0 suffices. Above a certain length, further increase has hardly any effect, but such a long inflow zone would result in very thick spinplates that are more difficult to make and handle. The inflow zone thus preferably has a L_0 /D_0 of at most 100, or at most 75, or 50. The optimum length depends on factors like molar mass of polyethylene, concentration, and flow speeds.

In a preferred embodiment of the process according to the invention a spinplate comprising at least 10 spinholes, each cylindrical spinhole having a inflow zone of constant diameter D_0 with L_0 / D_0 at least 10, at least one contraction zone with cone angle in the range 10-60°, and a downstream zone of constant diameter D_n with L_n / D_n at most 15 is applied, but also any other combination of indicated preferred embodiments is possible.

In the process according to the invention the fluid filaments can be further drawn upon leaving the spinhole, by applying a higher pick-up rate after cooling the filaments, than the flow rate upon leaving the spinhole. This stretching applied before solidification upon cooling is called the draw ratio in the air-gap DR_{ag}, and is in prior art also referred to as draw down. The DR_{ag} can be 1.0 if the pick-up rates equals the flow rate, but the draw ratio is generally optimised in combination with the applied DR_{sp} to reach a certain minimum DR_{fluid}. Preferably, the draw ratio in the air-gap is at

least 2, 5, or 10. The dimension of the air-gap appears not to be very critical, although it is preferably kept constant and the same for all filaments, and can be from some mm to several cm. If the air-gap is too long, molecular relaxation processes may annul part of the orientation obtained. Preferably, the air-gap is of about 5-50 mm length.

The fluid draw ratio DR_{fluid}, being DR_{sp} x DR_{ag}, that is applied to fluid filaments is at least 150, preferably at least 200, 250, or even at least 300. It is found that such a high draw ratio applied to fluid filaments results in improved drawability of the gel and dried filaments (DR_{solid}), and/or in improved tensile strength of the resulting yarn. This is also synonymous with improved processing stability of the process, since it reduces the chance that a filament is over-stressed at a certain draw ratio closely below the maximum, and thus reduces frequency of filament breakage. This is a surprising result, since experiments in prior art publications like WO 01/73173 A1 indicate that increasing the DR_{fluid} results in a lower draw ratio that can subsequently be applied to the solid filaments, and in lower tensile properties of the yarn.

The ultra-high molar mass polyethylene applied in the process according to the invention has an intrinsic viscosity (IV, as measured on solution in decalin at 135°C) of between about 8 and 40 dl/g, preferably between 10 and 30, or 12 and 28, more preferably between 15 and 25 dl/g. Intrinsic viscosity is a measure for molar mass (also called molecular weight) that can more easily be determined than actual molar mass parameters like M_n and M_w. There are several empirical relations between IV and M_w, but such relation is highly dependent on molar mass distribution. Based on the equation $M_w = 5.37 \times 10^4 [IV]^{1.37}$ (see EP 0504954 A1) an IV of 4 or 8 dl/g would be equivalent to M_w of about 360 or 930 kg/mol, respectively. Preferably, the UHPE is a linear polyethylene with less than one side chain per 100 carbon atoms, and preferably less than one side chain per 300 carbon atoms, a side chain or branch usually containing at least 10 carbon atoms. The linear polyethylene may further contain up to 5 mol% of one or more comonomers, such as alkenes like propylene, butene, pentene, 4-methylpentene or octene.

In a preferred embodiment, the UHPE contains a small amount of relatively small groups as side chains, preferably a C1-C4 alkyl group. It is found that a certain amount of such groups results in yarns having improved creep behaviour. Too large a side chain, or too high an amount of side chains, however, negatively affects the processing and especially the drawing behaviour of the filaments. For this reason, the UHPE preferably contains methyl or ethyl side chains, more preferably methyl side chains. The amount of side chains is preferably at most 20, more preferably at most 10

per 1000 carbon atoms.

The UHPE that is applied in the process according to the invention may further contain small amounts, generally less than 5 mass% of customary additives, such as anti-oxidants, thermal stabilizers, colorants, flow promoters, etc. The UHPE can be a single polymer grade, but also a mixture of two or more different grades, e.g. differing in IV or molar mass distribution, and/or number of side chains.

In the process according to the invention any of the known solvents suitable for gel spinning of UHPE can be used, for example paraffin wax, paraffin oil or mineral oil, kerosene or decalin. It is found that the present process is especially advantageous for relatively volatile solvents, like decalin and several kerosene grades. The solution of UHPE in solvent can be made using known methods. Preferably, a twin-screw extruder is applied to make a homogeneous solution from a UHPE/solvent slurry. The solution is preferably fed to the spinplate at constant flow rate with metering pumps. The concentration of the UHPE solution is between 3 and 25 mass%, with a lower concentration being preferred the higher the molar mass of the polyethylene is. Preferably, the concentration is between 3 and 15 mass% for UHPE with IV in the range 15-25 dl/g.

The UHPE solution is preferably of substantially constant composition over time, because this improves processing stability and results in yarn of more constant quality over time. With substantially constant composition it is meant that parameters like UHPE chemical composition and molar mass, concentration of UHPE in the solution, and chemical composition of the solvent vary within a certain range around a chosen value.

Cooling of the fluid filaments into solvent-containing gel filaments may be performed with a gas flow, or by quenching the filament in a liquid cooling bath after passing an air-gap, the bath preferably containing a non-solvent for the UHPE solution. If gas cooling is applied, the air-gap is the length in air before the filaments are solidified. Preferably a liquid quench-bath is applied in combination with an air-gap, the advantage being that drawing conditions are better defined and controlled than by gas cooling. Although called air-gap, the atmosphere can be different than air; e.g. as a result of an inert gas like nitrogen flowing, or as a result of solvent evaporating from filaments. Preferable, there is no forced gas flow, or only of low flow rate. In a preferred embodiment, the filaments are quenched in a bath containing a cooling liquid, which liquid is not miscible with the solvent and which flows along the filaments at least at the location where the fluid filaments enter the quench bath.

Solvent removal can be performed by known methods, for example by evaporating a relatively volatile solvent, by using an extraction liquid, or by a combination of both methods.

The process for making a polyethylene yarn according to the invention further comprises, in addition to drawing the solution filaments, drawing the filaments in at least one drawing step performed on the semi-solid or gel filaments and/or on solid filaments after cooling and at least partial removal of solvent, with a draw ratio of at least 4. Preferably, drawing is performed in more than two steps, and preferably at different temperatures with an increasing profile between about 120 and 155°C. A 3-step draw ratio applied on (semi-) solid filaments is represented as DR_{solid} = $DR_{solid\ 1}$ x $DR_{solid\ 2}$ x $DR_{solid\ 3}$; i.e. it is composed of the draw ratios applied in each drawing step.

It is found that a draw ratio DR_{solid} of upto about 35 can be applied, to reach the highest tensile properties of the yarn obtainable for a given DR_{fluid}. As a result of improved drawability and strength of partly drawn filaments in the process according to the invention, relatively high draw ratios, preferably in the range 5-30, may be applied without frequent filament breakage occurring, also depending on the applied draw ratio on fluid filaments. The process according to the invention thus results in multifilament HPPE yarn not only showing higher tensile strength than known multifilament yarns, but also less fluffing; especially if draw ratios have been optimised.

In a special embodiment according to the invention, a 3-15 mass% solution of linear UHPE of IV 15-25 dl/g is spun through a spinplate containing at least 10 spinholes into an air-gap, the spinholes comprising at least one contraction zone with a cone angle in the range 10-60° and comprising a zone of constant diameter D_n with a length/diameter ratio L_n / D_n smaller than 10 downstream of the contraction zone, while applying a fluid draw ratio DR_{fluid} = DR_{sp} x DR_{ag} of at least 200 and a draw ratio DR_{solid} of between 5 and 30; but also other combinations of said parameter settings provide good results.

The invention further relates to a spinplate comprising at least 5 spinholes of geometry and preferred features as defined and described above. The advantage of said spinplate is that, when applied in a process for making high-performance polyethylene multifilament yarn it enables a high degree of drawing on fluid filaments and a stable spinning process, resulting in yarn of increased strength and with high consistency in properties between individual filaments.

The invention further relates to a HPPE multifilament yarn that is obtainable by the process according to the invention, the yarn showing higher tensile strength than any known HPPE yarn containing at least 5 filaments. More specifically, the invention relates to an HPPE multifilament yarn containing n filaments that has a tensile strength of at least $5.8*(n^{-0.065})$ GPa, wherein n is at least 5, preferably to such yarn having a tensile strength of at least $6.0*(n^{-0.065})$, $6.2*(n^{-0.065})$ or even $6.4*(n^{-0.065})$ GPa. Preferably, the number of filaments in the yarn is at least 10, 50, 100, 150; 200 or even at least 300. Preferably, the said yarn is an as-spun yarn; meaning that the yarn is the direct product of a spinning and drawing process, and is not made by assembling yarn containing less filaments. Of course, the as-spun yarn according to the invention can further be assembled into yarns, or ropes etc, of higher titer or linear density without departing from the invention.

Such high-strength yarn is very useful for various applications, like making of heavy-duty ropes and cables, or for making ballistic-resistant composites with improved protection level, or reduced weight. Yarn of relatively low titer, but of extremely high strength is a.o. very suited for making high strength surgical fibres. The invention therefore specifically relates to a HPPE multifilament yarn containing at least 20 filaments, the yarn having a tensile strength of at least 5 GPa. Especially for making ropes, multifilament yarn of such high strength, which also shows an elongation at break of more than about 2.5% is advantageous, because of higher strength efficiency of such ropes. The invention therefore specifically relates to a HPPE multifilament yarn containing at least 200 filaments that has a tensile strength of at least 4.1 GPa and an elongation at break of at least 2.8%.

The invention further relates to various semi-finished and end-use articles containing the high-performance polyethylene multi-filament yarn according to the invention, or a high-performance polyethylene multi-filament yarn obtainable by the process according to the invention. Examples of such articles include various ropes and cords, fishing nets, sports equipment, medical applications, and ballistic-resistant composites. In most of these applications the tensile strength of the yarn is an essential parameter determining performance of the article.

Ropes especially include heavy-duty ropes for application in marine and offshore operations, like anchor handling, seismic operations, mooring of drilling rigs and production platforms, and towing. Preferably, such ropes contain at least 50 mass% of the yarn according to the invention, more preferably at least 75, or even 90 mass%. Most preferably, the rope consists essentially of HPPE yarn according to the

invention. Such products also show improved performance, like reduced creep and longer time to rupture under continuous loading conditions, in addition to higher strength. Products containing high amounts of HPPE yarn have a low relative density; possibly lower than water, which is an advantage in marine and offshore applications.

The invention further relates to a multi-layer ballistic-resistant assembly containing a plurality of mono-layers comprising HPPE yarn according to the invention, and to ballistic-resistant articles comprising such an assembly. The HPPE yarn can be present in various forms in a mono-layer, including woven and non-woven fabrics. Preferably, the mono-layers contain uni-directionally oriented HPPE filaments; with the fibre direction in each mono-layer being rotated with respect to the fibre direction in an adjacent mono-layer. The mono-layers may further comprise a binder material, basically to hold the filaments together. The binder material can have been applied by various techniques; for example as a film, as a transverse bonding strip or fibres (transverse with respect to the uni-directional filaments), or by impregnating and/or embedding the filaments with a matrix, e.g. with a solution or dispersion of matrix material in a liquid. The amount of binder material is preferably less than 30 mass% based on the mass of the layer, more preferably less than 20 or 15 mass%. The mono-layers may further comprise small amounts of auxiliary components, and may comprise other filaments. Preferably the mono-layers only comprise HPPE filaments as reinforcing fibres. Such mono-layers are therefore also referred to as mono-layers consisting essentially of HPPE filaments.

The multi-layer ballistic-resistant assembly can also be an assembly of at least two preformed sheet layers, a sheet layer comprising at least two mono-layers comprising high-performance fibres and a binder material, and optionally other layers, like a film or fabric; that have been consolidated or attached to each other. Such multi-layer ballistic-resistant assemblies or panels, and their manufacture are known in the art, for example from US 4916000, US 4623574, EP 0705162 A1 or EP 0833742 A1.

For so-called hard ballistic applications like vehicle armouring, rigid panels that have been (compression-) moulded from a plurality of mono-layers containing HPPE yarn are generally applied. For soft ballistic applications like body armour, flexible panels assembled from a plurality of mono-layers containing HPPE yarn, e.g. by stacking mono-layers or preformed sheets and securing the stack by for

example stitching at the corners or around the edges, or by placing inside an envelope, are preferred.

A multi-layer ballistic-resistant assembly containing mono-layers consisting essentially of HPPE yarn according to the invention shows surprisingly good anti-ballistic properties, exceeding the performance of known assemblies or panels. It is for example found that a flexible assembly that fulfils the NIJ II requirements (stopping of a 9 mm Parabellum FMJ (full metal jacket) bullet of 8.0 g with impact speed of 367 m/s, and a 0.357 Magnum JSP (jacketed soft point) bullet of 10.2 g at a speed of 436 m/s), has an areal density about 25% or more lower than that of a state-of-the-art panel. A reduced weight is a distinct advantage in both personal protection as in vehicle armouring and the like.

The invention more specifically relates to a ballistic-resistant assembly comprising a plurality of mono-layers consisting essentially of HPPE multifilament yarn, the assembly having an areal density (AD) of at least 1.5 kg/m^2 and a specific energy absorption (SEA) of at least 300 J.m^2/kg as measured against a 9x19 mm FMJ Parabellum bullet according to a test procedure based on Stanag 2920. Preferably, the assembly has a SEA of at least 325, or at least 350 J.m^2/kg. Areal density is expressed in mass per surface area, and is also referred to as areal mass or areal weight.

The invention is further elucidated by the following example and comparative experiments.

Methods

- IV: the Intrinsic Viscosity is determined according to method PTC-179 (Hercules Inc. Rev. Apr. 29, 1982) at 135°C in decalin, the dissolution time being 16 hours, with DBPC as anti-oxidant in an amount of 2 g/l solution, by extrapolating the viscosity as measured at different concentrations to zero concentration;
- Side chains: the number of side chains in a UHPE sample is determined by FTIR on a 2 mm thick compression moulded film, by quantifying the absorption at 1375 cm^{-1} using a calibration curve based on NMR measurements (as in e.g. EP 0269151);
- Tensile properties: tensile strength (or strength), tensile modulus (or modulus) and elongation at break (or eab) are defined and determined on multifilament yarns as specified in ASTM D885M, using a nominal gauge length of the fibre of 500 mm, a crosshead speed of 50%/min and Instron 2714 clamps, of type Fibre

Grip D5618C. On the basis of the measured stress-strain curve the modulus is determined as the gradient between 0.3 and 1% strain. For calculation of the modulus and strength, the tensile forces measured are divided by the titre, as determined by weighing 10 metres of fibre; values in GPa are calculated assuming a density of 0.97 g/cm^3.

- Ballistic performance: V50 and SEA of composite panels were determined with a test procedure according to Stanag 2920, using 9 mm *19 mm FMJ Parabellum bullets (from Dynamit Nobel). An assembly of layers was fixed using flexible straps on a support filled with Roma Plastilin backing material, which was preconditioned at 35°C.

Examples 1-2

A 6 mass% solution of a UHPE homopolymer having less than 0.3 side groups per 1000 per carbon atoms and an IV of 27.0 dl/g in decalin, containing a ratio of cis/trans isomers of between 38/62 and 42/58, was made, and extruded with a 25 mm twin screw extruder equipped with a gear-pump at a temperature setting of 180°C through a spinplate having 24 spinholes into a nitrogen atmosphere with a rate of 1.0 g/min per hole. The spinholes had an initial cylindrical channel of 3.0 mm diameter and L/D of 18, followed by a conical contraction with cone angle 45° into a cylindrical channel of 1.0 mm diameter and L/D of 10. The solution filaments were cooled in a water bath kept at about 35°C and with a water flow rate of about 5 cm/s perpendicular to the filaments entering the bath, and taken-up at such rate that a draw ratio of 15 was applied to the as-spun filaments in the air-gap of 15 mm. The filaments subsequently entered an oven at 130°C. The filaments were further stretched by applying a draw ratio of about 4, during which process the decalin evaporated from the filaments. The total draw ratio $DR_{overall}$ (= DR_{fluid} x DR_{solid}) amounted 1440. The yarn thus obtained had a tensile strength of 5.2 GPa and a modulus of 202 GPa. Relevant data is shown in Table 1.

In Example 2 the experiment was repeated, be it that a draw ratio in the semi-solid state of 5 was applied. As a result of the higher draw ratio, also higher tensile properties were found.

Comparative experiment A

In this experiment the draw ratio in the air-gap was lowered, resulting in a DR_{fluid} of 135. The measured tensile strength was significantly lower than for higher draw ratio.

Example 3

This experiment is performed analogously to the foregoing, with following modifications: the spinplate has an inflow channel of diameter 4,5 mm and L/D = 10, a contraction zone with cone angle 20°, and subsequent channel of diameter 0,3 mm and L/D of 5, resulting in a DR_{sp} of 225; the draw ratio in the air-gap is about 1.0 by matching take-up speed with flow speed. With the draw ratio applied to the solidified filaments set at 5, the resulting yarn shows extremely high tensile strength and modulus.

Comparative experiments B-C

In these experiments a solution of a UHPE polymer having less than 0.3 side groups per 1000 per carbon atoms and an IV of 19.8 dl/g in decalin was extruded with a 40 mm twin screw extruder equipped with a gear-pump at a temperature setting of 180°C through a spinplate having 195 spinholes into an air-gap with a rate of 2.2 g/min per hole. The spinholes had the same geometry as in Ex 1-2, but with cone angle 60°. In exp. B an 8 mass% solution was used, in exp. C 9 mass%. The water in the quench bath was kept at 30-40°C, and had a flow rate of about 3 cm/s near the filaments. Solid-state drawing was performed in two steps, first with a temperature gradient of about 110-140°C and than at about 151°C. The draw ratio in the air-gap could not be increased too much without processing instabilities occurring (filament breakage), unlike in e.g. Ex. 1, which may be related to the lower molar mass UHPE used. The resulting yarn had a strength comparable with known yarns, see Table 1 and Fig. 2.

Examples 4-5

The same spinning and drawing equipment and conditions as in Comp. Exp. B-C were used, but with a spinplate having an inflow channel of diameter 3.5 mm and L/D = 18, a contraction zone with cone angle 60°, and subsequent channel of diameter 1.0 mm and L/D of 10, resulting in a DR_{sp} of 12.25. The spin rate was 1.7 g/min per hole. The draw ratio in the air-gap could be increased, resulting in stable production of very high strength yarn, see Table 1 and Figure 2.

Example 6

Example 4 was repeated with a spinplate having 195 holes of similar geometry, but with a cone angle of 30°.

Comparative experiments D-F

Analogously to Comparative experiments B-C a yarn was made, but with a spinplate containing 390 spinholes of same geometry. HDPE solution was 8, 8 and 9 mass% respectively. The experimental results were also highly comparable; the yarn showing slightly lower tensile strength as expected for the higher number of filaments.

Examples 7-10 and Comparative experiment G

Using the same set-up and conditions as in comp. Exp. D, yarns were spun applying a spinplate having 390 spinholes of geometry as in Ex 4-5. In Ex. 10 the spinrate was lowered to 1.7 g/min per hole. Again, a high draw ratio could be applied to the fluid filaments, resulting in very good tensile properties; see Table 1 and Fig. 2. If the DR_{fl} was decreased by applying a relatively small draw ratio in the air-gap, tensile strength dropped significantly (Comp. Exp. G).

Examples 11-12

Multifilaments yarns were spun from a decalin solution containing 8 mass% of UHPE of IV 19.8 dl/g, using a 130 mm twin-screw extruder equipped with a gear-pump through spinplates containing 588 spinholes having an inflow zone of diameter 3,5 mm and L/D of 18, a conical contraction zone with cone angle 60°, and subsequent capillary with diameter 0.8 mm and L/D 10. The draw ratio in the spinholes was thus 19.1; the draw ratio in the air-gap was 16.2 and 18.1 (at spinrates 2.2 and 2.0 g/min per spinhole). Water flow rate in the cooling bath was about 6 cm/s. The tensile properties of the yarns are in agreement with yarns produced under similar conditions but containing less filaments (see Table 1 and Figure 2).

Example 13

The experiment of Example 11 was repeated, but with similar spinplates containing 1176 spinholes. Multifilament yarns containing1176 filaments having very high tensile strength could be produced with high processing stability.

Comparative Experiment H

The experiment of Comp. Exp. F was repeated, but with the spinplate containing 780 spinholes; and essentially the same results.

Examples 14-16

Using the experimental set-up and conditions of Ex. 4, yarns were spun from a 7 mass% solution of UHPE of IV 21,4 and less than 0.3 side groups per 1000 per carbon atoms, with a spinrate of 1,7 g/min per spinhole. The tensile strength of the yarns obtained were somewhat higher than of comparable products made from

lower molar mass UHPE.

In Figure 2 the tensile strengths as measured in all above experiments have been plotted versus the logarithm of the number of filaments in the respective yarn. Also included are data points from the experiments reported in WO 01/73173, as well as those from Figure 1. It is clearly seen that the Examples 1-16 display higher strength than the known yarns and yarns made in Comp. Exp. A-H, and the strength values are at least $5.8*(n^{-0.065})$ GPa with n at least 5; which formula is represented in Figure 2 by the bold line.

Example 17

The multifilament yarn of Example 13, having a titer of 930 dtex, was used to make a uni-directional (UD) mono-layer by feeding the yarn from several packages from a creel, spreading the filaments, and impregnating the filaments with an aqueous dispersion of Kraton® D1107 stryrene-isoprene-styrene blockcopolymer as matrix material. After drying the UD mono-layer had an areal density of 22.2 g/m^2 and a matrix content of about 23 mass%. Four (4) of these mono-layers of 40 x 40 cm size were stacked cross-wise (fibre direction in each layer at an angle of 90° with direction in adjacent layer), a polyethylene film of about 7 g/m^2 was placed on both sides of the stack, and the package was consolidated by compressing at about 110°C and about 0.5 MPa. The areal density of this preformed sheet was 103.8 g/m^2.

A number of these sheets were stacked, and the assembly was stabilized by some stitches at each corner. The ballistic performance of the assembly was tested with 9 mm parabellum bullets (see above). In Table 2 the results are collected for assemblies with 3 different areal densities.

Examples 18-19

Example 17 was repeated, but the mono-layers now had AD 20.2 g/m^2 and matrix content 15 mass% (Ex. 18). Ex 19 was made with the yarn of Example 11 of 465 dtex, the mono-layer had AD of 18.4 g/m^2 and 15 mass% of matrix. More details are given in Table 2.

Comparative experiment I

Analogously to Ex. 17 assemblies were made from a commercial multifilament HPPE yarn (Dyneema® SK76 1760 dtex), containing 780 filaments and with TS 3.5 GPa. The mono-layer had an AD of 32.8 g/m^2 and a matrix content of 18 mass%.

From the data in Table 2 it is clear that the panels made with a yarn

according to the invention show significantly better ballistic performance in relation to their areal density. In Figure 3 this is further illustrated by plotting the V50 values, the velocity at which the estimated probability that a bullet will perforate the panel is 50 %, versus areal density for Ex. 17-19 and Comp. exp. I.

Example 20.

A UD mono-layer was made as in Ex 17 with AD of 37.6 g/m^2 and matrix content of about 10 mass%. A preformed sheet was made by placing two mono-layers cross-wise with a polyethylene film of 7 g/m^2 on both sides, and consolidating by compression. The AD hereof was 89.2 g/m^2.

A number of these sheets were stacked, stabilized with stitches, and tested on anti-ballistic performance as before.

Examples 21-22

Starting from a mono-layer with AD 40.3 g/m^2 and 15 mass% of matrix, Ex 20 was repeated.

In Ex. 22 the experiment of Ex 20 was repeated, but 4 instead of 2 mono-layers were placed cross-wise and consolidated into a sheet.

Comparative experiment J

Monolayers and sheet were made as in Comp. Exp. I. The mono-layer had an AD of 58.5 g/m^2 and a matrix content of 16 mass%.

The results shown in Table 2 show that also for assembled panels of structure differing form Ex17-19, the panels made from yarn according to the invention have significantly better protection level at the same areal density than panels according to the state of the art. In Figure 4 this is further illustrated by plotting the V50 values versus areal density.

Table 1.

	n	DR_{sp}	DR_{ag}	*Air-gap*	DR_{fluid}	DR_{solid}	$DR_{overall}$	*TS*	*Modulus*	*eab*
				(mm)				*(GPa)*	*(GPa)*	*(%)*
ex 1	24	9	40,0	15	360	4	1440	5,2	202	
ex 2	24	9	40,0	15	360	5	1800	5,3	208	
comp A	24	9	15,0	15	135	5	675	3,2	140	
ex 3	24	225	1,0	5	225	5	1125	5,6	203	
comp B	195	9	4,4	15	40	34	1346	3,6	128	2,86
comp C	195	9	12	20	108	20	2160	3,7	126	3,27
ex 4	195	12,25	25,2	45	309	24,4	7532	4,3	168	3,01
ex 5	195	12,25	33,5	50	410	25,2	10341	4,8	182	2,96
ex 6	195	12,25	25,2	45	309	25,2	7779	4,5	170	3,04
comp D	390	9	4,4	15	40	32	1267	3,4	126	2,82
comp E	390	9	10,2	20	92	33,6	3084	3,4	114	2,97
comp F	390	9	12	20	108	20	2160	3,6	121	3,24
ex 7	390	12,25	14,6	35	179	24,4	4364	3,9	162	3,07
ex 8	390	12,25	19,4	40	238	18,9	4492	4,0	136	3,12
ex 9	390	12,25	20,0	40	245	21,6	5292	4,1	157	3,07
ex 10	390	12,25	25,2	45	309	24,4	7532	4,2	166	2,98
comp G	390	12,25	2,2	10	27	28	755	2,7	84	2,86
ex 11	588	19,1	16,2	25	309	25,2	7797	4,2	155	2,98
ex 12	588	19,1	18,1	25	346	25,2	8712	4,3	153	3,05
comp H	780	9	12	20	108	20	2160	3,4	114	3,23
ex 13	1176	19,1	16,2	25	309	25,2	7797	4,1	151	3,02
ex 14	195	12,25	25,2	45	309	25,2	7779	4,6	175	3,03
ex 15	390	12,25	20,1	40	246	25,2	6205	4,3	154	3,05
ex 16	390	12,25	25,2	45	309	25,2	7779	4,5	171	3,02

Table 2

	Preformed sheet		Assembled sheets			
	number of mono-layers	AD (g/m^2)	number of sheets	AD (kg/m^2)	ballistic results V50 (m/s)	SEA ($J.m^2/kg$)
Ex. 17	4	103,8	20	2	407	322
			27	2,8	456	300
			33	3,4	487	280
Ex. 18	4	94	21	2	425	365
			30	2,8	466	307
			36	3,4	489	280
Ex. 19	4	86	23	2	441	391
			33	2,8	482	324
			40	3,4	496	288
Comp. I	4	145	18	2,6	415	265
			24	3,4	468	258
			30	4,3	493	226
Ex. 20	2	89,2	22	2	322	211
			31	2,6	435	272
			38	3,4	466	245
Ex. 21	2	95	21	2	333	201
			29	2,6	426	263
			36	3,4	458	245
Ex. 22	4	176	11	2	375	291
			16	2,6	455	296
			19	3,4	501	310
Comp. J	2	131	23	3	392	236
			26	3,5	417	205
			30	4	460	213

CLAIMS

1. Process for making high-performance polyethylene multifilament yarn comprising the steps of
a) making a 3-25 mass% solution of ultra-high molar mass polyethylene having an intrinsic viscosity as measured on solutions in decalin at 135°C of between about 8 and 40 dl/g, in a solvent;
b) spinning of the solution through a spinplate containing at least 5 spinholes into an air-gap to form fluid filaments, while applying a draw ratio DR_{fluid};
c) cooling the fluid filaments to form solvent-containing gel filaments;
d) removing at least partly the solvent from the filaments; and
e) drawing the filaments in at least one step before, during and/or after said solvent removing, while applying a draw ratio DR_{solid} of at least 4,
characterized in that
in step b) a fluid draw ratio $DR_{fluid} = DR_{sp} \times DR_{ag}$ of at least 150 is applied, wherein DR_{sp} is the draw ratio in the spinholes and DR_{ag} is the draw ratio in the air-gap, with DR_{sp} being greater than 1 and DR_{ag} at least 1.

2. Process according to claim 1, wherein the spinhole has a geometry comprising a contraction zone, with a gradual decrease in diameter from diameter D_0 to D_n with a cone angle in the range 8-75°, and wherein the spinhole comprises a zone of constant diameter D_n with a length/diameter ratio L_n/D_n of from 0 to at most 25 downstream of a contraction zone.

3. Process according to any one of claims 1-2, wherein the cone angle is from 10 to 60°.

4. Process according to any one of claims 1-3, wherein the draw ratio in the spinholes is at least 2.

5. Process according to claim 4, wherein the draw ratio in the spinholes is at least 10.

6. Process according to any one of claims 1-5, wherein the spinhole further comprises a zone of constant diameter D_n downstream of a contraction zone, this zone having a length/diameter ratio L/D_n of at most 20.

7. Process according to claim 6, wherein the ratio L/D_n is at most 15.

8. Process according to any one of claims 1-7, wherein the spinhole further comprises an inflow zone of constant diameter of at least D_0, with a ratio L_0 / D_0 of at least 5.

9. Process according to claim 8, wherein the ratio L_0 / D_0 is at least 10.

10. Process according to any one of claims 1-9, wherein a spinplate comprising at least 10 spinholes, each cylindrical spinhole having a inflow zone of constant diameter D_0 with L_0 / D_0 at least 10, a contraction zone with cone angle in the range 10-60°, and a downstream zone of constant diameter D_n with L_n / D_n at most 15 is applied.

11. Process according to any one of claims 1-10, wherein the fluid draw ratio DR_{fluid} applied to fluid filaments is at least 250.

12. Process according to any one of claims 1-11, wherein a 3-15 mass% solution of linear UHPE of IV 15-25 dl/g is spun through a spinplate containing at least 10 spinholes into an air-gap, the spinholes comprising a contraction zone with a cone angle in the range 10-60° and comprising a zone of constant diameter D_n with a length/diameter ratio L_n / D_n smaller than 10 downstream of a contraction zone, while applying a fluid draw ratio $DR_{fluid} = DR_{sp} \times DR_{ag}$ of at least 200 and a draw ratio DR_{solid} of between 5 and 30.

13. High-performance polyethylene multifilament yarn having a tensile strength of at least $5.8*(n^{-0.065})$ GPa, wherein the number of filaments n is at least 5.

14. High-performance polyethylene multifilament yarn containing at least 20 filaments, the yarn having a tensile strength of at least 5 GPa.

15. High-performance polyethylene multifilament yarn according to claim 13 or 14, wherein n is at least 150.

16. High-performance polyethylene multifilament yarn containing at least 200 filaments having a tensile strength of at least 4.1 GPa and an elongation at break of at least 2.8%.

17. Semi-finished and end-use articles containing the high-performance polyethylene multi-filament yarn according to any one of claims 13 - 16.

18. Ballistic-resistant assembly comprising a plurality of mono-layers consisting essentially of high-performance polyethylene multifilament yarn, the assembly having an areal density of at least 1.5 kg/m^2 and a specific energy absorption of at least 300 J.m^2/kg as measured against a 9 * 19 mm FMJ Parabellum bullet according to a test procedure based on Stanag 2920.

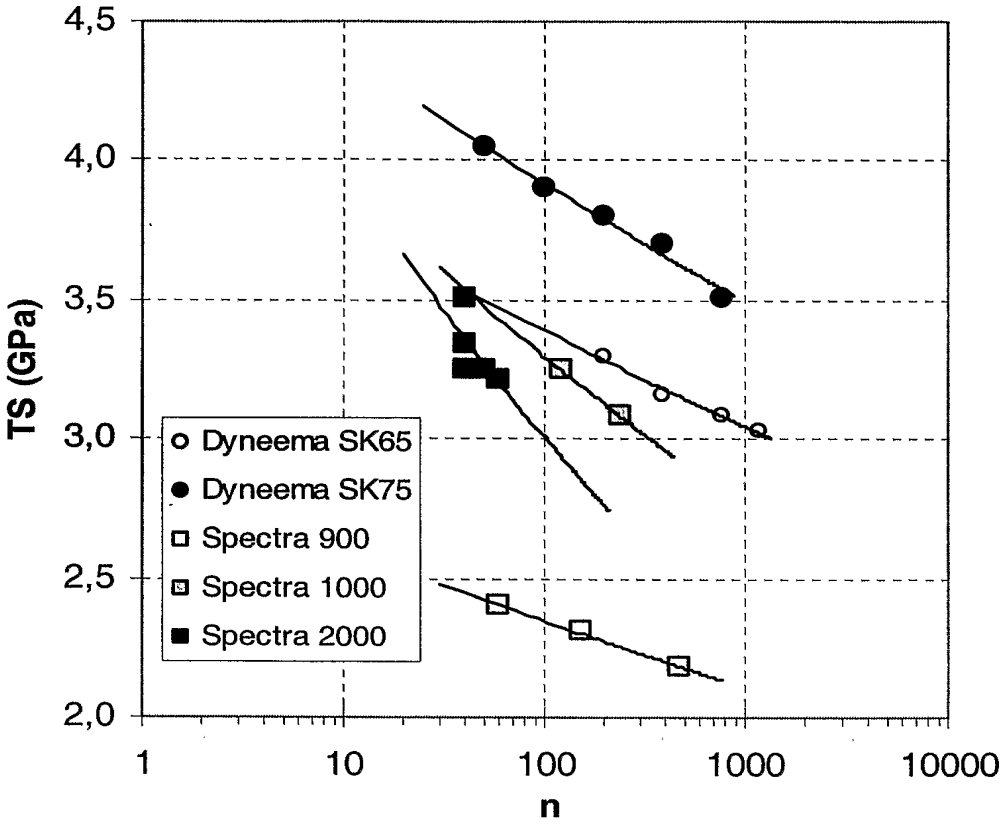
19. Ballistic-resistant assembly according to claim 18, wherein the mono-layers contain uni-directionally oriented filaments, with the fibre direction in each mono-layer being rotated with respect to the fibre direction in an adjacent mono-layer.

20. Ballistic-resistant assembly according to any one of claims 18-19, wherein the specific energy absorption of the panel is at least 325 $J.m^2/kg$.

PCT/NL 2004/000029

ABSTRACT

The invention relates to a process for making high-performance polyethylene multi-filament yarn comprising the steps of a) making a solution of ultra-high molar mass polyethylene in a solvent; b) spinning of the solution through a spinplate containing at least 5 spinholes into an air-gap to form fluid filaments, while applying a draw ratio DR_{fluid}; c) cooling the fluid filaments to form solvent-containing gel filaments; d) removing at least partly the solvent from the filaments; and e) drawing the filaments in at least one step before, during and/or after said solvent removing, while applying a draw ratio DR_{solid} of at least 4, wherein in step b) a draw ratio $DR_{fluid} = DR_{sp} \times DR_{ag}$ of at least 150 is applied, with DR_{sp} being the draw ratio in the spinholes and DR_{ag} the draw ratio in the air-gap, and DR_{sp} being greater than 1 and DR_{ag} at least 1. The invention further relates to a high-performance polyethylene multifilament yarn, and to semi-finished or end-use products containing said yarn, especially to various kinds of ropes and ballistic-resistant composites.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2,5
2,0
TS (GPa)
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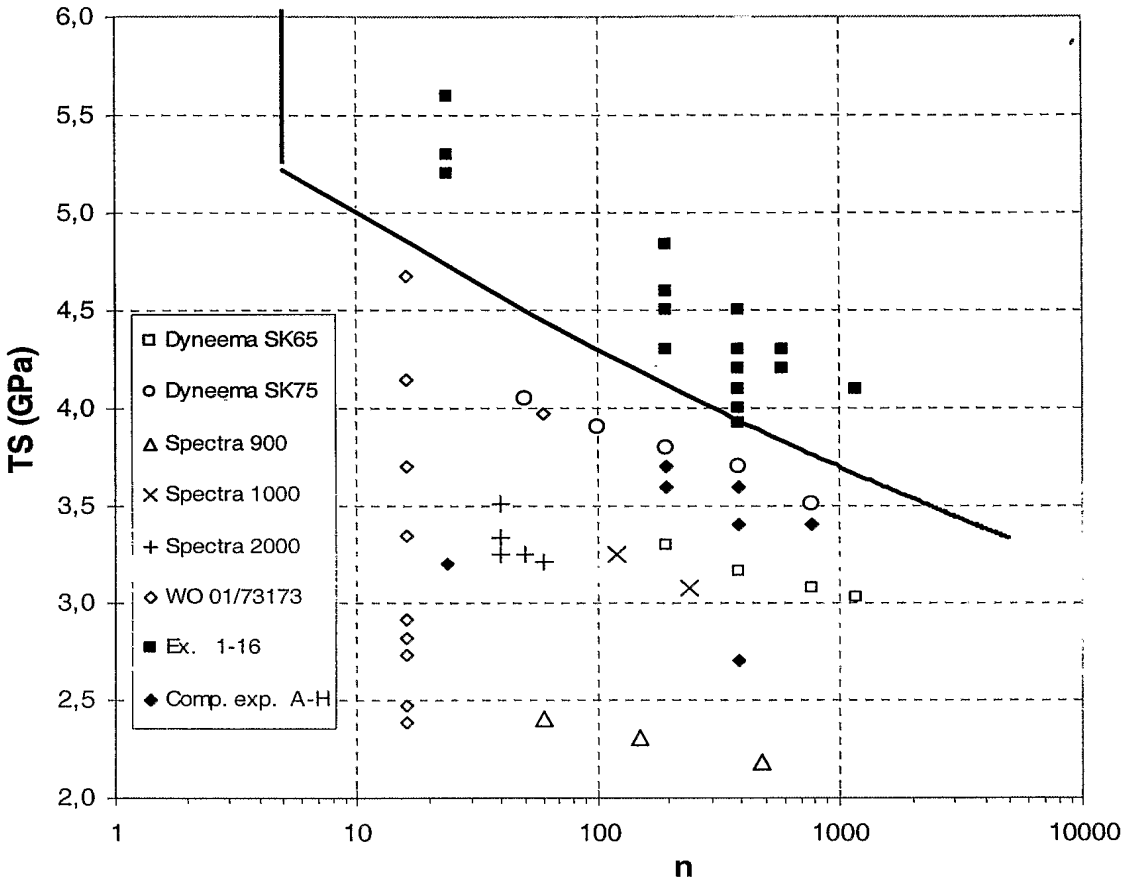
10
100
1000
10000
n
Dyneema SK65
Dyneema SK75
Spectra 900
Spectra 1000
Spectra 2000

Fig. 1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1000
10000
n
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WO 01/73173
Ex. 1-16
Comp. exp. A-H

Fig. 2

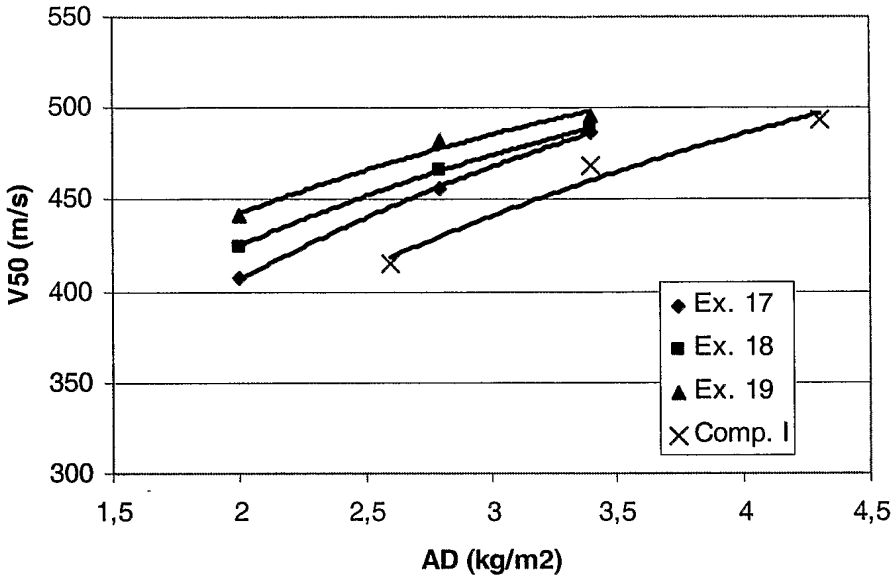
550
500
450
400
350
300
V50 (m/s)
1,5
2
2,5
3
3,5
4
4,5
AD (kg/m2)
Ex. 17
Ex. 18
Ex. 19
Comp. I

Fig. 3

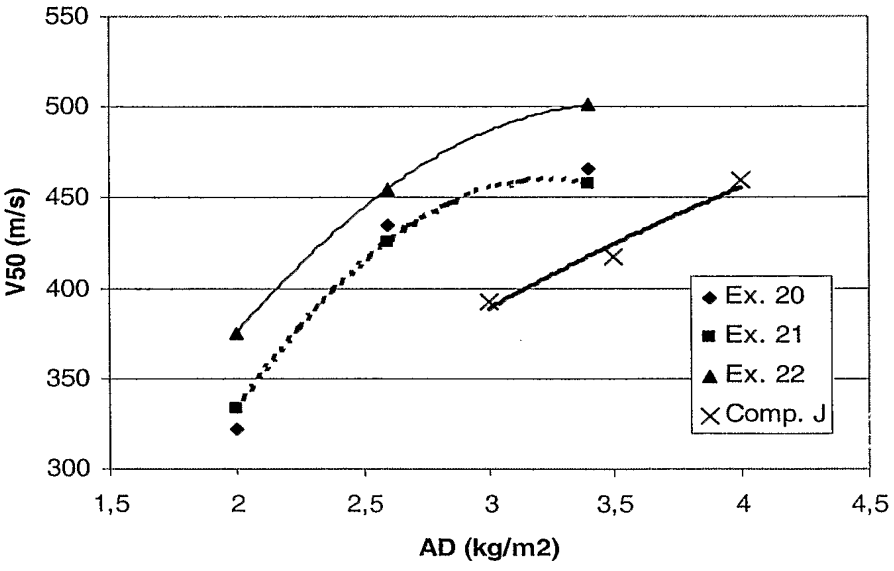
550
500
450
400
350
300
V50 (m/s)
1,5
2
2,5
3
3,5
4
4,5
AD (kg/m2)
Ex. 20
Ex. 21
Ex. 22
Comp. J

Fig. 4